arbon isotope evidence for the stepwise xidation of the Proterozoic environment

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oxidation of the Earth's crust and the increase in atmospheric oxygen early in Earth history have n linked to the accumulation of reduced carbon in sedimentary rocks. Trends in the carbon isotope mposition of sedimentary organic carbon and carbonate show that during the Proterozoic aeon –0.54 Gyr ago) the organic carbon reservoir grew in size, relative to the carbonate reservoir. This ease, and the concomitant release of oxidizing power in the environment, occurred mostly during isodes of global rifting and orogeny.

HAPS life's most extensive alteration of its environment es from the splitting of the water molecule during oxygenic tosynthesis to produce molecular oxygen (O_2) and reducing er for the synthesis of organic matter

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$

his environmental alteration became extensive when part of O_2 escaped back-reaction with organic matter (CH_2O in the tion above), because some of the organic matter was buried diments and thus removed. Therefore O_2, sulphate (SO_4^{2-}) ferric iron (Fe^{3+}) accumulated in the crust and atmosphere ly because organic matter and biogenic sulphide accumud in sediments[1,2]. Even biogenic sulphide owes its existence ly to sedimented organic matter, which fuels bacterial ction of sulphate. Oxidation of the Earth's surface environnt was thus promoted not by biological processes alone, but their interaction with geological processes such as imentation.

The history of oxidation during the Proterozoic aeon can be ed by quantifying the growth of the crustal organic carbon rvoir[2,3]. Each mole of organic carbon represents a mole of that either still exists or has reacted with some oxidizable stance. Most important among the latter are Fe^{2+} and uced sulphur. The delivery of these to the surface environnt is also controlled by geological processes.

With these factors in mind, we present here the results of a rdinated study of the Earth's biogeochemical and tectonic ords. We have used new data and have taken into account cesses occurring since the initial deposition of the organic terial. Probable rates of deposition and recycling of sediments ve been considered. We find that oxidation of the environment proceeded very unevenly and that the main transitions are related with geological rather than biological events.

ss balances within the carbon cycle

ble isotope analyses of carbonate and organic matter offer most effective approach for tracing the growth of the stal reservoir of reduced carbon. Natural abundances ^{13}C in marine sedimentary carbonates ($\delta_{carb} = (^{13}C/^{12}C)_{carb}/(^{13}C/^{12}C)_{standard} - 1$) and in organic matter (δ_{org}) controlled by (1) equilibrium isotope effects among inorganic bon species, (2) isotopic fractionations associated with the ynthesis and reworking of organic matter, and (3) the relarates of immobilization and burial of carbonate and organic bon in sediments. The isotopic difference between buried bonate carbon and organic carbon, $\Delta_c = \delta_{carb} - \delta_{org}$, is there- an indicator of processes within the global carbon cycle. Isotope effects associated with the enzymatic fixation of carbon and with mass transport of CO_2 are responsible for most of Δ_c. The overall fractionation accompanying photosynthesis can be attenuated by limitations in the supply of CO_2 (refs 4, 5). The amounts of carbonate and organic carbon buried depend on global rates of erosion and sedimentation[6] and on recycling processes at the sea floor[7]. The operation of the carbon cycle can be monitored through an isotopic mass balance

$$\delta_{in} = f_{carb}\delta_{carb} + f_{org}\delta_{org} \quad (1)$$

where δ_{in} represents the isotopic composition of carbon entering the global surface environment comprised of the atmosphere, hydrosphere and biosphere, and the right side of the equation represents the weighted-average isotopic composition of carbon being buried in sediments, f_{carb} and f_{org} being the fractions of carbon buried in inorganic and organic form ($f_{carb} = 1 - f_{org}$). Carbon enters the surface environment by weathering, volcanism and rock metamorphism and, over timescales longer than 100 Myr, $\delta_{in} = -5‰$, the average value for crustal carbon[8]. Where values of sedimentary δ_{carb} and δ_{org} can be measured, it is thus possible to determine f_{org} for ancient carbon cycles (all δ values in ‰)

$$f_{org} = (\delta_{in} - \delta_{carb})/(\delta_{org} - \delta_{carb}) = (\delta_{carb} + 5)/\Delta_c \quad (2)$$

The carbon isotopic record

Strauss *et al.*[9] summarized 731 isotope analyses (Fig. 1) of total organic carbon in Proterozoic sediments. Except for some new low values for rocks older than 2.6 Gyr, the $\delta^{13}C$ values from earlier work and the new study do not differ substantially. Lines tracing the average values of δ_{carb} and δ_{org} in Fig. 1 are roughly parallel, creating the impression that Δ_c was invariant throughout the Proterozoic. Some authors have therefore emphasized aspects of uniformity in the Proterozoic carbon cycle and its isotope record[10–12]. Episodic $\delta^{13}C$ variations have, however, been found[13,14].

The δ_{org} values in Fig. 1 reflect not only biological and palaeoenvironmental effects, but also postdepositional thermal degradation of the kerogen, which results in preferential loss of ^{13}C-depleted, hydrogen-rich products. As a result, changes in the H/C ratio and δ_{org} of residual kerogens are correlated[15]. As would be expected, older kerogens are more likely to be thermally altered and have lower H/C ratios[16]. Because δ_{org} has been affected, the true magnitudes of Δ_c and f_{org} during the Proterozoic have been obscured.

To minimize isotopic shifts due either to extreme thermal alteration or to analytical artefacts, Fig. 2 includes isotopic

compositions[9,17] only for kerogens with ash contents less than 25% and H/C values greater than 0.1. Furthermore, the best view of the Proterozoic isotopic record can be obtained by reconstructing the values of δ_{org} before alteration. The characteristic trend relating changes in δ_{org} to values of H/C has been examined in detail[15,18]. Relationships between changes in H/C and changes in δ_{org} are not significantly dependent on kerogen type or host lithology[17]. The curve which relates the most probable values for this shift ($\Delta\delta_{org}$) to H/C values (see Fig. 5-5 of ref. 17) has the form

$$\Delta\delta_{org} = 4.05 - 3.05r + 0.785/r + 0.0165/r^2 - (8.79\times10^{-4})/r^3 \quad (3)$$

where $\Delta\delta_{org} = \delta_{org}$ (as analysed, H/C = r) − δ_{org}(initial, H/C = 1.5). When initial δ values are reconstructed, the isotope record takes the form shown in Fig. 2. Because δ_{carb} is relatively constant, the changes in Δ_c must, as shown by equation (2), be linked principally to changes in f_{org}.

Burial of organic carbon

When the data of Fig. 2 are used to calculate values of f_{org} for 100-Myr increments between 2.5 and 0.6 Gyr, results indicate a long-term increase (Fig. 3). Complementary changes in δ_{carb} and δ_{org} (Fig. 2) support this trend. This increase was not monotonic but episodic; high values were attained between 2.1 and 1.8 Gyr and between 1.1 and 0.7 Gyr. These changes will have affected the total crustal inventory of organic carbon and, in turn, other aspects of the surface redox environment.

Computed values of f_{org} indicate the average degree of reduction of carbon being stored in accumulating sediments. At the extremes, $f_{org} = 0$ corresponds to no reduction (all carbon being buried as carbonate) and $f_{org} = 1$ corresponds to complete reduction (all carbon being buried as organic). This output of carbon from the surface environment is balanced by inputs contribu by erosion and thermal activity. These carbon inputs will b least partly reduced, because they include organic carbon b remobilized during destruction of older sediments. If the ave degree of reduction of the output differs from that of the in there must be a net transfer of oxidizing or reducing power f the carbon cycle to the cycle of some other element, presum iron, sulphur or oxygen.

To reconstruct changes in the crustal inventory of org carbon during the Proterozoic, we have begun by postula that the f_{org} value observed at 2.6 Gyr accurately reflects ca burial before that time. If so, the crust then contained a $0.09\times7.6\times10^{21}$ mole organic carbon ($=f_{org}\times C_{tot}$, where C the total number of moles of carbon in the crust[11]). Durin next 100 Myr, the time interval between 2.6 and 2.5 Gy fraction of the crustal inventory of carbon will have recycled, passing through the surface reaction chamber being reburied with the f_{org} value characteristic of that e Quantitatively, variations in the organic carbon reservoi then be calculated as follows

$$M_{t-\tau} = M_t\, e^{-k\tau} + C_{tot}(1 - e^{-k\tau})f_{org}$$

where M is the quantity of organic carbon in the crust, t present age of sediments deposited at the beginning increment (t approaches 0 as time advances), τ is the dur of the increment, f_{org} is based on δ values observed durin interval t to $t-\tau$, and k is the first-order decay constant ch teristic of the recycling of the sedimentary inventory. sediment half life of 400 Myr (ref. 19), $k = (\ln 2)/$ 1.733 Gyr^{-1}. The first term on the right of equation (4) repre survival of crustal organic carbon from one time increme the next, the second represents effects of recycling. Ste application of this equation yields the results summariz Fig. 4.

Uncertainties in M can be discussed mainly in terms k parameter. First, k is certainly time-variant. Tectonic ations strongly influence rates at which crustal materia recycled[19]. Rates of erosion and, thus, rates of burial of sed

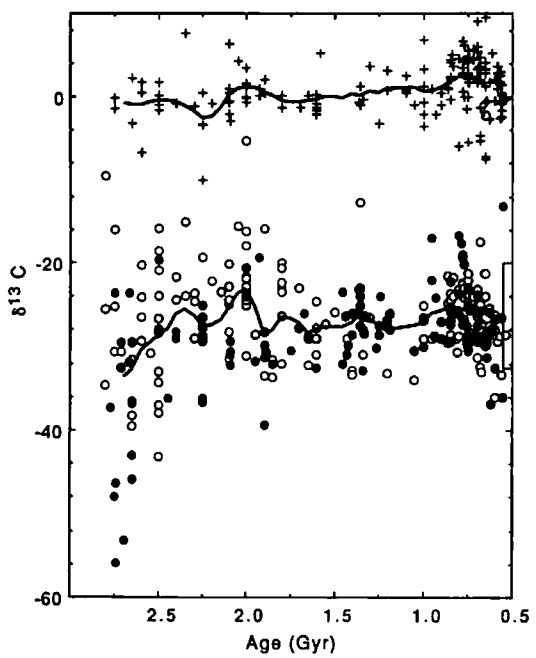

FIG. 1 δ_{carb} (crosses) and δ_{org} (circles) against age of unpurified kerogens. ●, Values obtained by Strauss *et al.*[9]; ○, earlier data (see Strauss *et al.*[9] for compilation). Solid lines depict running averages, calculated for successive 100-Myr time increments, of 200 Myr intervals during the Proterozoic. For example, a δ value given for 1.0 Gyr is an average of values between 1.1 and 0.9 Gyr. The rectangle located midway along the right margin represents the range of δ_{org} values typically observed in Phanerozoic sediments[60].

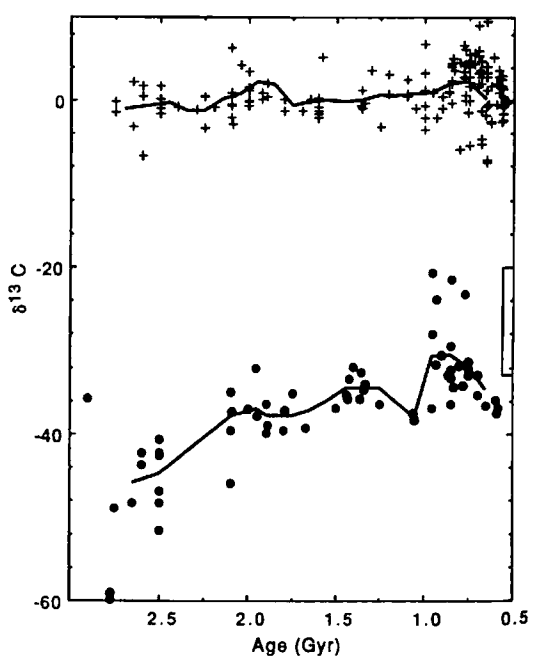

FIG. 2 δ_{carb} (crosses) and δ_{org} (circles) against age of purified ke δ_{org} values are corrected for postdepositional alteration (see text Fig. 1, the solid lines depict running averages of the data, and the re along the right margin of the figure represents Phanerozoic δ_{org} va

tary debris, and/or whe weathering Proterozoic, can be interp and burial. T variations in 0.3 Gyr and

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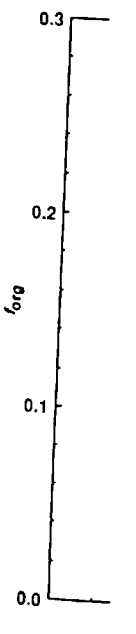


FIG. 3 Fraction of ca purified kerogens. Re of enhanced global ri

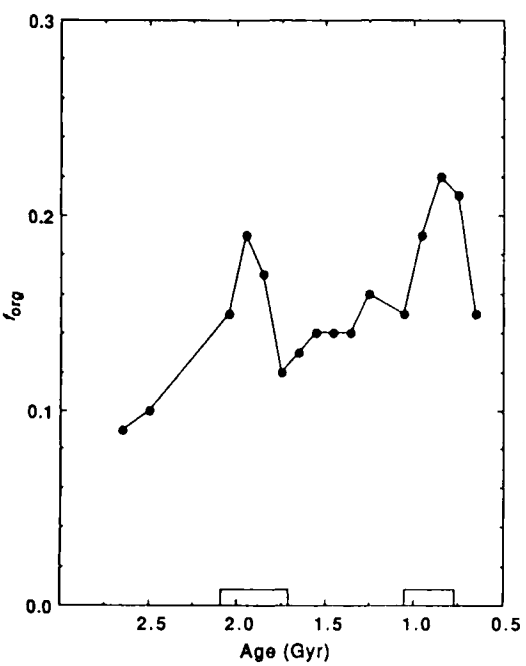
debris, are highest when high mountain terrain is extensive or when continental plates experience rifting. Rainfall and weathering are also important and are variable. For the late Proterozoic, the isotopic records of strontium and neodymium are interpreted[6] in terms of large variations in rates of erosion and burial. To examine the sensitivity of our estimates of M to variations in k, we have also considered sediment half lives of 1 Gyr and 0.5 Gyr (Fig. 4).

A second uncertainty related to k concerns the postulate that $M_{2.6}$ (the value 2.6 Gyr ago) can be estimated from f_{org} prevailing at that time. This estimate does seem at least to be representative of organic sedimentation during the interval 2.7 to 2.5 Gyr (Fig. 3). We have not used the entire isotopic record before 2.5 Gyr to estimate variations in M from the beginning of the rock record, because the earlier record is incomplete and highly altered.

Values of δ_{carb} have been affected to some extent by postdepositional alteration of carbonates, yet no corrections have been made here. Because of their greater age, early Proterozoic carbonates might be more affected than late Proterozoic carbonates. Veizer *et al.*[20] obtained a 'corrected' δ_{carb} value of 0 ± 1.5‰ for early Proterozoic marine carbonate, which is in reasonable agreement with the corresponding average δ_{carb} values in Fig. 2. Apparently, postdepositional alteration of carbonates has not seriously compromised the accuracy of the calculations of M.

Episodic release of oxidizing power

Assuming a half life of 0.4 Gyr we find that M increased in the Proterozoic mostly in two increments as follows: from 0.7×10^{21} to 1.05×10^{21} mol between 2.5 and 1.8 Gyr, and from 1.05×10^{21} to 1.3×10^{21} mol between 1.3 and 0.7 Gyr. It is instructive to explore both the causes of this trend in M and also its consequences for crustal and atmospheric abundances of oxidized species such as Fe^{3+}, SO_4^{2-} and O_2. Rates of organic burial depend not only on the intensity of production of biomass but also on the preservation of organic matter as it is delivered to sediments and awaits burial. Productivity depends on the efficiency and environmental tolerance of photoautotrophs and on the delivery of nutrients to the photic zone[3,21]. Organic preservation depends on the versatility and aggressiveness of heterotrophs, on the availability of oxidants in the water column and sediments, and on the rate of sedimentation of inorganic debris, rapid burial assisting preservation[22,23]. Thus both productivity and preservation are affected by both biological and geological processes. Although the evolutionary development of oxygenic photosynthesis must have enhanced productivity because it allowed autotrophs to make use of an abundant and ubiquitous electron donor, this evolutionary step occurred during the Archean[24-27], at least 600 Myr before the time when, according to geochemical evidence, O_2 accumulated in the atmosphere. Thus the pulses of accelerated organic burial revealed by the Proterozoic record are expected to correlate with time intervals during which tectonically enhanced rates of weathering and erosion delivered more nutrients[28] and promoted rapid burial.



3 Fraction of carbon buried as organic matter (f_{org}) against age of fied kerogens. Rectangles along the bottom margin depict time intervals enhanced global rifting and orogeny (see text).

Most of the O_2 generated from the photosynthetic production of organic matter is consumed by respiratory processes. The small amount of organic matter that escapes oxidation by being buried (today, ~0.2-0.3% of primary production[7,29]) allows an equivalent amount of O_2 to remain in the surface environment[1]. Burial of organic carbon thus releases O_2; erosion commonly exposes organic carbon, sulphide, and Fe^{2+} which consume O_2 (refs 2, 3, 30). It is instructive to explore how this balance was affected by tectonic events during the Proterozoic.

Proterozoic events

The interval 3.0 to 2.4 Gyr probably saw the first assembly of large, relatively stable continental plates from smaller cratons[31], setting the stage for extensive cratonic sedimentation[32]. Carbonate platforms having most of the essential features of their Phanerozoic equivalents were well developed by 2.6 to 2.3 Gyr (ref. 33). Indeed, the best-developed Proterozoic carbonate platforms, with evidence of extensive oxygenic photosynthetic stromatolitic communities, are primarily of early Proterozoic age[33]. This evidence for extensive production of O_2 might seem to conflict with the observation from palaeosols that O_2 levels were low before 2.0 Gyr (ref. 34). But modern microbial mats remineralize organic matter efficiently (D. E. Canfield and D.J.D., manuscript submitted); the low amounts of organic carbon in early Proterozoic stromatolitic carbonates[35] are thus not unexpected. Oxidants can be consumed as rapidly as they are produced in these communities. Little organic carbon was buried on the extensive early Proterozoic carbonate platforms, so net accumulation of O_2 was near zero. This picture is consistent with the low values of f_{org} (0.1) observed for the earliest Proterozoic (Fig. 3). The smaller net production of oxidants was probably consumed by reactions in sea-floor hydrothermal systems[36], which were more active then than today. Accordingly, seawater SO_4^{2-}, although present, was substantially below modern concentrations[37]. The deposition of Superior-type banded iron formations at that time apparently required an anoxic deep ocean[3] containing some dissolved Fe^{2+}.

Commencing at 2.2-2.1 Gyr, the large continental plates that had assembled for the first time in the late Archean to early Proterozoic underwent rifting and, later, orogeny on a global scale, as evidenced by massive basic and ultrabasic dyke swarms and Andean-type orogenic belts[31]. Post-Archean tectonic cycles display an increasingly prominent early rift stage and a well-developed terminal stage of orogeny[32]. Accordingly, rifting on a global scale probably promoted the development of extensive anoxic basins favourable for organic preservation. A sustained rise in seawater $^{87}Sr/^{86}Sr$ values at that time[38] indicates enhanced rates of continental erosion. The earliest-known glaciations occurred during this interval[39], lowering the sea level, exposing more continent, and making conditions more favourable for high rates of erosion and clastic sedimentation[40]. Between 2.1 and 1.7 Gyr, the opening and closing of Atlantic-type ocean basins caused rifting and uplift which accelerated the rates of erosion, release of nutrients for biological production,

near-shore sedimentation and, therefore, organic burial. One such episode of enhanced organic sedimentation at this time might be represented by ^{13}C-rich carbonates reported by Baker and Fallick[14].

The idea that growth of the crustal inventory of reduced carbon (M) led to oxidation of other elements is supported by geological evidence. A substantial rise in atmospheric O_2 levels is indicated by increase in retention of Fe^{3+} in palaeosols[34,41] and emergence of extensive redbeds[42]. The biosynthesis of sterol precursors requires O_2, and the oldest known sterane biomarkers occur in the 1.69 Gyr Barney Creek formation[43]. The deposition of Superior-type banded iron formations was curtailed severely after 1.8 Gyr (ref. 44), perhaps because of oxygenation of the deep ocean. Possibly the oldest known occurrence of massive SO_4^{2-} evaporite deposition is recorded in 1.4–1.8-Gyr sediments of the McArthur basin, Australia[45].

During the interval 1.7 to 1.2 Gyr, orogenic activity was not as globally extensive as it was during the preceding period. There is no evidence of glaciation[39]. A supercontinent may have existed, orogenic activity was more local in nature, and terms such as 'anorogenic magmatism' and 'abortive rifting' have been used to characterize major tectonic events of that time[31]. It is reasonable to conclude that global rates of sedimentation and organic burial were low to moderate. The absence of evidence for large changes in the sizes of the oxidized reservoirs is therefore not surprising. The O_2 content of the atmosphere was apparently maintained at a value intermediate between modern levels and those of the early Proterozoic[46].

Tectonic activity increased during the interval 1.2 to 0.9 Gyr. The emplacement of extensive mafic dyke swarms[31] heralded the breakup of the supercontinent and the wide dispersal of continental fragments[47,48]. Modern-style orogenic cycles[31] and glacial episodes[39] became more frequent than before. Once again conditions were favourable for relatively rapid rates of organic sedimentation. Massive evaporites occur during and after this interval in central Africa (Upper Roan group[49]), North America (Grenville series[50]) and Australia (Bitter Spr formation[51,52]).

As indicated in Fig. 4, the crustal organic carbon reser increased in a stepwise fashion during each of the two intervals during the early and middle-to-late Proterozoic, w global rifting and orogenies occurred. A third stepwise incr apparently occurred in a brief interval between the Varan glacial eposide and the Cambrian boundary[6]. These event not correlated with the development of new biological sou of O_2. Indeed, the last stepwise oxidation is correlated with development of important new O_2 consumers, the metazo It is instead likely tht these increases were driven by accele rates of erosion, nutrient release and clastic sedimenta factors that are known to accelerate organic sedimentation the modern Earth[29,30]. These observations support earlier posals that tectonic events strongly affected the biogeochem carbon[40] and sulphur[53] cycles. That the oxidized crustal re voirs of O_2, SO_4^{2-} and Fe^{3+} also increased, as predicted supported by evidence which is particularly compelling for interval 2.1 to 1.8 Gyr (ref. 41). A prediction from the pre findings is that a second large increase in the oxidized reserv occurred between 1.1 and 0.8 Gyr. A systematic search for s evidence should be undertaken.

The role of life

These findings challenge the widely held view that innovati in biological evolution directed the long-term rise of atmosph oxygen levels. As stated earlier, the development of oxyg photosynthesis occurred at least 600 Myr before O_2 (accor to geochemical evidence) accumulated in the atmosphere. E eukaryotic organisms, which require O_2 for biosynthesis essential lipids[54], appear in the palaeontological record ab 2.1 Gyr ago[55], perhaps before the first large O_2 increase discu here. Photosynthesis indeed provided an O_2 source str enough to sustain a major atmospheric increase, but the tim and magnitude of O_2 accumulation was regulated by tecto processes controlling erosion and sedimentation. These obse tions are consistent with the view[19,56] that chemical prope of the environment that are buffered by large crustal reserv (such as crustal organic carbon and sulphur) over long ti scales (>10 Myr) will ultimately be controlled by geolog processes, such as tectonics, which regulate interactions those reservoirs.

The growth of the crustal organic carbon reservoir and resultant oxidation of the surface environment must have p foundly affected the Earth's biota. Evidence of abundant euk otic organisms appears in the organic geochemical record ab 1.7 Gyr ago[43]. Because eukaryotes require O_2, it is logica associate an increase in their abundance and diversity with rise of O_2 that probably accompanied the growth of the org reservoir between 2.2 and 1.8 Gyr.

The declining $\delta^{13}C$ difference between sedimentary carbo and reduced carbon during the Proterozoic (Fig. 2) sug that isotopic discrimination during biological CO_2 up decreased in response to declining CO_2 concentrations in oceans and atmosphere[9]. The fact that the greatest declin discrimination coincides with the episodes of global rifting orogeny is consistent with the drawdown of atmospheric C levels which accompanies high erosion rates[57]. It is theref likely that the atmospheric ratio of O_2 to CO_2 increased marke during these episodes. Evolutionary changes in the enzy ribulose bisphosphate carboxylase oxygenase[58,59], which both CO_2 and O_2 as substrates, might have been triggered these transitions.

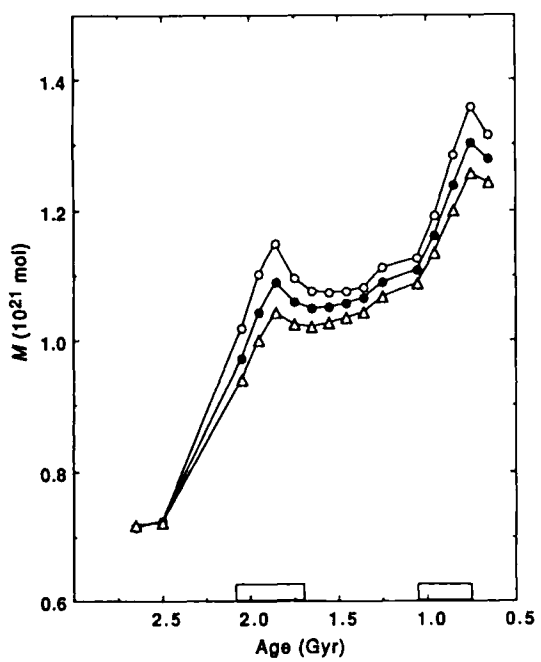


FIG. 4 Quantity of organic carbon in the crust (M) against age. Values of M are calculated according to equation (4) (in the text). Symbols represent calculations of M, assuming sediment half lives (see derivation of equation (4) as follows : ○, 300 Myr; ●, 400 Myr; △, 500 Myr. Rectangles along the bottom margin depict time intervals of enhanced global rifting and orogeny (see text).

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truncated activin receptor inhibits esoderm induction and formation f axial structures in *Xenopus* embryos

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...tivins can induce mesoderm in embryonic explants and have been proposed as the natural inducer ...*Xenopus*. A mutant activin receptor that inhibits activin signalling is used to show that activin is ...uired for the induction of mesoderm *in vivo* and the patterning of the embryonic body plan. Blocking ... activin signal transduction pathway also reveals autonomous induction of a neural marker and ...masks a relationship between activin and fibroblast growth factor.

...DERSTANDING the processes that lead from a fertilized egg ...e formation of germ layers and subsequently to a body plan ... central goal of embryology. Much of what is known about ...development of a vertebrate body plan comes from studies ...mphibia where, at the tadpole stage, the main body axis ...ists of the dorsal structures notochord, spinal cord and ...ites organized anterior to posterior as head, trunk and tail. ...animal tissues derive from the three germ layers and the ...oderm plays a pivotal role in organizing the body axis[1]. ...odermal cells lead the movements of gastrulation[2,3], are ...uired for the patterning of the nervous system[4,5], and them-...es give rise to the muscular, skeletal, circulatory and excre-... systems. Moreover, a portion of the dorsal mesoderm from ...y gastrula, the Spemann organizer, can induce and organize ...cond body axis following transplantation to another site[6]. ...understanding of the development of mesoderm will help ...clarify how the vertebrate body plan is generated.

Before gastrulation the three germ layers are simply arranged, top to bottom, in a frog blastula. Ectoderm arises from the top, or animal pole; mesoderm from the middle, or marginal zone, and endoderm from the bottom or vegetal pole. Mesoderm can be induced in animal pole cells (animal caps) by signals emanating from the vegetal pole[7]. Several peptide growth factors have been identified that can induce mesoderm in animal caps *in vitro*. When animal cap tissue is explanted from a blastula embryo and cultured in isolation it develops into a ball of epidermis. But in the presence of an inducing factor, the animal cap will differentiate into mesodermal derivatives, including notochord, muscle and blood[8,9]. Members of the fibroblast growth factor family, in particular basic fibroblast growth factor (bFGF)[10,11], and the transforming growth factor-β (TGF-β) family[12], notably activins[13–15], are potent inducers in this assay. *Xenopus* homologues of the *Wnt* gene family may also have a role in mesoderm induction. Both *Xwnt1* (ref. 16) and *Xwnt8*